

An analysis of photoemission and inverse photoemission spectra of Si(111) and sulphur-passivated InP(001) surfaces

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Photoemission (PES) and inverse-photoemission spectra (IPES) for the sulphur-passivated InP(001) surface are compared with theoretical predictions based on density-functional calculations. As a test case for our methods, we also present a corresponding study of the better known Si(111) surface. The reported spectra for InP(001)-S agree well with the calculated ones if the surface is assumed to consist of a mixture of two phases, namely, the fully S-covered (2×2) -reconstructed structure, which contains four S atoms in the surface unit-cell, and a (2×2) structure containing two S and two P atoms per unit cell. The latter has recently been identified in total-energy calculations as well as in core-level spectra of S-passivated InP(001) surfaces under annealing. The experimental IPES for Si(111)- (2×1) is in excellent agreement with the calculations. The comparison of the experimental-PES with our calculations provides additional considerations regarding the nature of the sample surface. It is also found that the commonly-used density-of-states approximation to the photo- and inverse- photoemission spectra is not valid for these systems.

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I. INTRODUCTION

The sulphur-treated indium phosphide surface, InP(001)-S, has recently attracted much attention, where the effort towards a microscopic understanding of the physics has been spurred by its technological importance in surface passivation problems.¹⁻³ This surface has been studied experimentally using a variety of methods, including X-ray absorption near-edge spectroscopy,⁴ Raman spectroscopy,⁷ core-level spectroscopy (CLS),^{5,6,8} photoemission (PES) and inverse photoemission (IPES) spectroscopy,⁹ low-energy electron diffraction (LEED),¹⁰ and scanning tunneling microscopy (STM).¹¹ Theoretically, it has been examined in detail using total energy minimization based on density-functional theory (DFT).^{7,8}

Early studies suggested that the InP(001)-S surface is a (1×1) structure that follows the bulk (zinc-blende) pattern, terminated with the sulphur atoms on the bridge sites (see for instance Refs. 4 and 10). The actual situation, however, has turned out to be much more complicated. Thus, LEED data on samples annealed at 350°C appeared to have a clear (2×1) pattern.⁹ However, Raman experiments and theoretical calculations indicated⁷ that the “as-prepared” low-temperature material arranges into a novel (2×2) structure with *two* types of sulphur on the surface, as displayed in Fig. 1. This structure has four sulphur atoms on the surface unit-cell, belonging to two distinct sublayers about 0.2 Å apart; the bottom sublayer is dimerized, i.e., contains a S₂ “molecule”, while the top sublayer consists of two S atoms in a monomer state. We will refer to this surface

as the S₂SS structure.

Further theoretical calculations, combined with CLS measured as a function of the annealing temperature of the surface, showed that other surface structures were allowed within a given thermal window. The most important of these forms *via* the exchange of surface-sulphur atoms with bulk-phosphorous atoms which migrate to the surface.⁸ It was demonstrated that the most-likely structure in the 300–400°C annealing range is a (2×2) -reconstruction containing essentially *one* type of sulphur, with the surface layer containing equal amounts of S and P atoms that form tight S–P bonds (Fig. 2) which are slightly tilted so that the P-atoms are on top of the surface. We will refer to this structure as (SP)₂. At much higher temperatures, all the surface sulphur gets replaced by phosphorous, leading to a P-terminated sulphur-free InP(001) surface. Although the (SP)₂ structure is a (2×2) -reconstruction, it could easily appear to be (2×1) if LEED fails to distinguish between S and P atoms. Thus, we are lead to a picture wherein the InP(001)-S surface is actually a system which could contain a mixture of S₂SS, (SP)₂, and the P-terminated InP(001) structure, depending on the kinetics imposed by the annealing conditions.

The objective of this paper is to examine the reported PES and IPES data for the samples annealed at 350°C by comparing them with first-principles DFT calculations of PES and IPES for the energetically-likely surface structures. It turns out that the best fit to the data is obtained by assuming that the surface is in a mixed phase consisting of S₂SS and (SP)₂ patches. In order to “benchmark” our calculations, we present similar calculations for the

(2 × 1)-reconstructed Si(111) surface. The spectra for Si(111)-(2 × 1) available in the literature are for samples prepared by cleavage in *vacuo*.¹² These spectra also contain various features which could arise from surface imperfections or even the presence of some admixture of the more stable (7 × 7) reconstruction. We have examined these issues within our analysis of the reported PES-spectra of Si(111), and they serve as a testing ground of the theoretical methods used here.

The plan of the paper is as follows. We first present, in Section II, the essentials of the theory. In Section III, we start by discussing our results for the Si(111) surface and compare them with the experimental data of Himpsel *et al.*¹² In particular, we emphasize that the PES and IPES spectra are *not* well accounted for by the density of states (DOS) of occupied or unoccupied levels. However, good agreement with theory is obtained when the calculation is done using the transition matrix elements obtained from the Kohn-Sham energy bands. We then proceed to a study of the InP(001)-S case and find that it is not possible to explain the experimental PES data in terms of a single-phase surface; however, we find good agreement if the surface is assumed to consist of a mixture of S₂SS and (SP)₂ phases which have been identified in annealing experiments.

II. THEORY

The geometrical details of the S₂SS and (SP)₂ structures described above were determined within the framework of DFT total-energy minimization calculations; full details can be found in Refs. 7 and 8. Given these structures, as in our previous studies, we construct supercells containing typically 16 atomic layers and the equivalent of 5 layers of vacuum. In the case of the Si(111) slab, the top and bottom 4 layers of the slab have the experimental geometry of the 2×1 reconstruction, while the middle eight layers have the bulk-Si geometry. These supercells are then used to calculate the electronic energy states (band structure) of these systems. We use, for this purpose, the all-electron, full-potential-linear-muffin-tin-orbital (FP-LMTO) method;¹⁶ in this formalism, the wavefunctions $\psi(\vec{r})$ are of the form:

$$\psi_i^{\vec{k}}(\vec{r}) = \sum_{t,L,K} C_{t,L,K}^n \chi_{t,L}^{\vec{k}}(E, K, \vec{r}), \quad (1)$$

where n is the band index and \vec{k} is the electron wavevector; t , L , K , and E are, respectively, the index of the atomic species in the unit cell, the angular momentum, the Hankel function expansion parameter (with $K^2 = -|\epsilon|$), and the reference energy E of the Bloch basis $\chi_{t,L}^{\vec{k}}$.¹⁶

The transition probability between initial and final states, $\psi_i(\vec{r})$ and $\psi_f(\vec{r})$, induced by the electron-photon interaction H_{int} is given by the Fermi golden rule as

$$W_{if} = \frac{2\pi}{\hbar} |\langle f | H_{int} | i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (2)$$

where $\hbar\omega$ is the photon energy. For PES, electrons with final energy E_f will escape from the sample with kinetic energy $E_{kin} = E_f - E_F - \phi$, where ϕ is the workfunction. The interaction Hamiltonian is $\vec{A} \cdot \vec{p}$, where \vec{A} is the vector potential of the photon field. In many cases, it is necessary to replace the external field due to the vector potential \vec{A} of the photons by the total field inclusive of induced fields using a Sternheimer-type procedure, as shown for instance by Zangwill and Soven.¹⁷ However, in our calculations, we restrict ourselves to the spectrum given by the simplest form of the Fermi golden rule. The velocity form of the matrix was used in the numerical calculations. The total photoelectron current per unit solid angle in PES is then

$$J^{PES}(E_{kin}, \omega) \propto \sqrt{E_{kin}} \sum_i W_{if}. \quad (3)$$

The expression for the transition probability for IPES is identical to PES; the IPES current is given by

$$J^{IPES}(E_{kin}, \omega) \propto [1/\sqrt{E_{kin}}] \sum_f W_{fi} \quad (4)$$

where, in this case, $E_{kin} = E_i - E_F - \phi$.

Rather than evaluating explicitly the transition matrix elements $\langle f | \vec{A} \cdot \vec{p} | i \rangle$, it is often assumed, for simplicity, that these are constant in the range of the energies concerned. In this approximation, the PES/IPES intensities become proportional to the DOS of occupied/unoccupied levels. Another approximation that is made in this context is to assume that the final electron state in PES (or the initial electron state in IPES) is a single plane-wave state. In reality, the final state in PES is probably more like a superposition of plane-waves dictated by the crystal potential and is best represented by the full, self-consistent, Kohn-Sham eigenfunction corresponding to the energy of the final state. It should be noted that the Kohn-Sham eigenvalues are well known to be a poor approximation to the quasi-particle energies, but the eigenfunctions themselves are generally a good approximation to the quasi-particle wave-functions. Thus, in the present study, we treat the PES and IPES calculations as separate problems dealing with separate experiments (as they indeed are), and do not attempt to relate them to each other, or to the experimental surface bandgaps; rather, we determine explicitly the Kohn-Sham eigenstates appropriate to the occupied/unoccupied levels, and use these to evaluate in detail the transition matrix elements of Eqs. (3) and (4). In fact, the DOS profile is found to yield poor approximations to the measured spectra. This fact is of some importance since experimental PES/IPES results are often presented as a “mapping” of the “band-structure” of a material, and theoretical bandstructures are often “corrected” to fit in with the PES-dispersions, without deconvoluting the effect of the matrix elements

and the non-plane wave character of the final (or initial) states in PES (or IPES).

In our numerical calculations, the δ -functions appearing in Eq. 2 and related equations will be replaced by a Lorentzian functions of width 0.2 eV. In calculating the matrix elements, the wavefunction given in Eq. 1 was expanded in plane-waves for ease of computation. An energy cutoff of 20 Ry was found to be sufficient for the spectral range studied, while test calculations using 30 Ry were performed in order to establish convergence in the expansions. Calculations were carried out for bulk Si, Si(111)-(2 \times 1), the S₂SS and (SP)₂ surface phases, and bulk InP. Since we are dealing with admixtures of several phases, i.e., surfaces which may only have short-range order, calculations are reported only for the $\bar{\Gamma}$ point of the surface Brillouin zone. It was verified that increasing the number of “bulk-like” layers in the simulation supercells helped to augment the bulk-like signal in the theoretical spectra, arising from the projected bulk DOS at the surface’s $\bar{\Gamma}$ point. Indeed, since light penetrates many atomic layers, the experimental spectra contain, to some extent, contributions from the bulk, as well as from resonances due to interactions among the surface and bulk excitations. In fact, one effect of coupling a surface slab to the bulk is to broaden all the peaks. This is similar to the effect of the Lorentzian broadening of the delta-functions used here. Also, by considering a sufficient number of bulk-like layers, we ensure that such effects are represented in the theory. Thus we checked for the convergence of the density of states in each layer as a function of slab thickness by considering systems containing up to 16 layers. The surface unit cell was always taken to be (2 \times 2); that is, no calculations were performed for the P-terminated InP surface free of sulphur resulting from high temperature annealing, which has a (2 \times 4) structure, or for the Si(111)-(7 \times 7) surface which is also considered in some of the discussions.

III. RESULTS AND DISCUSSION

In order to establish the reliability of our approach, we first consider the well-known Si(111) surface as a test case. We compare the results available in the literature with our theoretical calculations and return to the problem of interest here, viz. the InP(001)-S surface.

A. PES and IPES for the Si(111) surface

The Si(111)-(2 \times 1) surface was extensively studied in the early eighties and its spectroscopy played a pivotal role in eliminating the early models in favour of Pandey’s π -bonded chain structure.^{12,18–21} We use here some of the published spectra for the nominal Si(111)-(2 \times 1) surface as a benchmark for our calculations.

Fig. 3 compares our calculations for the IPES using the Kohn-Sham transition matrix elements (solid line), and DOS for unoccupied levels (dashed line), with the experimental results of Himpsel¹³ (squares) for the Si(111)-(2 \times 1) surface. Here we used a computational supercell consisting of a 16-layer slab of Si and 5 layers of vacuum. The absolute position of the theoretical curve was displaced to conform with the energy scale reported in the experiment. The Fermi energy of the (2 \times 1) surface is given, experimentally, to be 0.33 eV above the valence band maximum and this has been used in positioning the experimental spectrum. It is clear that the IPES calculation using the simple Fermi golden rule and the *full* matrix elements is in excellent agreement with experiment, while the corresponding DOS calculation is a poor representation of the experimental spectrum.

In Fig. 4, we present our calculated PES (dashed line) and DOS (dotted line) results for the Si(111)-(2 \times 1) surface, the calculated bulk PES signal (dot-dashed lined), as well as the experimental results of Himpsel *et al.*¹² We have not subtracted off the secondary-electron background in displaying the experimental spectra. The Si(111)-(2 \times 1) samples used in the experiments were cleaved under vacuum and believed to be single-phase material. However, scanning tunneling microscopy (STM) and other surface analysis techniques that are currently available were not available then.

It is clear from Fig. 4 that the PES calculation recovers the peaks at ~ -1.45 and ~ -0.7 eV seen in the experiment. (The DOS calculation also has features qualitatively similar to the experiment). However, the large, broad intensity seen around ~ -3.0 eV, is *not* reproduced by the PES or the DOS calculation. This -3 eV broad peak (3eVBP) is less prominent in the experimental PES curves reported in subsequent work.²¹ The bulk spectrum at the $\bar{\Gamma}$ -point shows a peak near -3.5 eV and -5.5 eV. It is very well known that perfect-cleavage surfaces of Si are very difficult to obtain. It has been suggested that the 3eVBP is a result of angle-integrated photoemission from bulk Si, scattered into the normal direction by surface imperfections.²² An additional reason for getting part of the angle-integrated spectrum superimposed on the angle-resolved spectrum is the effect of diffuse light scattering in the optical detection system of the particular analyser used in this specific experiment.²²

How the angle-integration of the bulk signal by surface imperfections can lead to a 3eVBP can be understood within the context of another possible explanation of the 3eVBP that we have explored. The Si(111) 2 \times 1 structure is metastable with respect to the 7 \times 7 reconstruction. There is no evidence suggesting that the (2 \times 1) surface reconstructs to the (7 \times 7) form at room temperature. However, the energy dumped on the surface by the 21 eV photon beam (and the secondary electrons etc., generated during the PES) may lead to local annealing of the surface structure. Such locally-annealed patches may exist in a surface which has already been used for, say IPES, and then used for obtaining the PES spec-

trum. Hence, we have also explored the possibility that the surface may contain (7×7) patches, now known to be the ground-state of Si(111).

In order to explore this possibility, we show in Fig. 5 the experimental angle-resolved PES from Si(111)- (7×7) for small angles in the range 0-10 deg. We need to consider only small angles here because the 7×7 -phases formed by relaxation of the 2×1 phase would be expected to have a set of small orientations which averages to zero with reference to the original 2×1 -surface. Further, the $\bar{\Gamma}$ point, common to both (2×1) and (7×7) surfaces, samples only photoelectrons that are normal to the surface. The averaged signal from the (7×7) surface for small angles does show the correct behaviour, giving a 3eVBP. When the secondary electron-tail is removed, this broad band is seen to be a small, but non-negligible, component of the whole spectrum. Hence, one possible explanation of the 3eVBP near ~ -3.0 eV would be that (7×7) patches are present in the cleaved sample believed to be (2×1) .

The angle-integration of the bulk signal by surface imperfections is clearly very analogous to the integration of the angle-resolved (7×7) data which contain multiple features in the -5 eV to -2.5 eV range and in the same manner can lead to a 3eVBP spectral feature. This explanation of the 3eVBP has the merit of not having to invoke the existence of 7×7 -reconstructed patches in the cleaved Si(111) sample.

Nevertheless, all these lead us to emphasize the importance of having data from truly well-characterized, clean surfaces when relating theory to experiment. Further, we note that even if PES and IPES experiments were carried out using the same sample, it may still be necessary to consider local-annealing of the surface and change of structure when going from one probe to another.¹⁴ Based on the above discussion and Fig. 3, we are led to conclude that the sample in IPES – at least the surface region probed by the experiment – was essentially a (2×1) region.

B. PES and IPES for the InP(001)-S surface

In contrast to Si, the InP surfaces are much less understood; this is true in particular of InP(001)-S. Obtaining good STM images or LEED for the as-prepared surface has been difficult. The LEED from the as-prepared surface is very poor and the photoemission is almost isotropic, indicative of poor structural order. In our Raman study of the problem, we recognized these difficulties and examined the signal arising from the phonons associated with the splitting of the *underlying* P-layer (just below the In-layer) induced by the surface reconstruction.¹⁵ Unlike the outermost-S layer, this inner-P layer was expected to be less influenced by surface contamination. PES and IPES experiments have been carried out with annealed samples characterized using LEED. However,

our study of the core-level spectra of these samples under annealing showed that the thermal treatment introduces new complications by favouring mixed-component phases containing a half-S-half-P-terminated surface.⁸ Thus, samples annealed at low temperatures for a short time (e.g., ~ 5 -10 min.) could easily be an admixture of the InP(001)-S₂SS and InP(001)-(SP)₂ phases. The former is the lowest-energy structure for full S coverage, while the latter is the structure favoured under annealing when bulk-P atoms migrate to replace the S-atoms which, in turn, diffuse into the bulk. When higher temperatures are used in annealing, the completely P-terminated InP(001) phase which is free of sulphur also becomes possible.

Fig. 6(a) presents our calculation of the PES for both the S₂SS (full line) and the (SP)₂ (dashed line) reconstructions of the InP(001)-S surface. Also included in this figure is the spectrum from bulk InP, projected onto the surface $\bar{\Gamma}$ point (dotted line). The experimental data of Mitchell *et al.*⁹ are displayed as squares in Fig. 6(b). The PES spectra of each phase (and the bulk) were separately calculated and aligned to have the same *d*-electron peak arising from In atoms (which are not significantly affected by surface reconstructions).

It is clear from Fig. 6 that neither the S₂SS spectrum nor the (SP)₂ spectrum, alone, can account for the experimental data, i.e., the measured spectrum evidently contains features from both surface phases. In order to show this clearly, we display as the full line in Fig. 6(b), a composite spectrum obtained by assuming that the region of the surface sampled by the light contains a mixture of S₂SS and (SP)₂, in proportions of 30% and 70% respectively. The composite spectrum was positioned (by a rigid shift of the x-axis) to the experimental spectrum and scaled to match the intensity of the most prominent peak. Clearly, a reasonable fit to the experimental data can be obtained in this way. The experimental spectrum will depend on details of sample preparation and annealing history. However, an invariant property would be that a composite theoretical spectrum constructed from the spectra of the three main annealing components, i.e., S₂SS, (SP)₂ and P-terminated InP(001), can always be found to match the essential features of a given experimental spectrum.

We are therefore led to conclude that the samples examined by Mitchell *et al.*⁹ using PES actually contain a mixture of S₂SS and (SP)₂ phases. This conclusion is in agreement with the observation that the width of the features in the experimental PES of InP(001)-S is found to be much broader than from cleaved GaAs or InP(110) surfaces.²³

Fig. 7 presents the results of our IPES calculations for a sample containing the same mixture of S₂SS and (SP)₂ phases as we have just discussed. It is of course not evident that the IPES experiments were carried out using the same sample that was used for the PES, i.e., with no further aging or surface modification, and therefore the surface structure need not be identical. Even with

identical samples, the regions of the surface probed by the photons in PES, and electrons in IPES need not be identical. The agreement between the calculation and the experiment, in fact, is very unsatisfactory in the region between 2.5 and 5.5 eV, where the theory predicts a low intensity. However, the fully P-terminated InP(001) surface is also a possible product of the annealing process and may be a component of the surface. The PES and STM of the P-terminated InP(001) has been studied recently.^{24,25} Experiment shows that this phase has a prominent broad absorption band just in the region 2.5–5.5 eV (dashed curve; Ref. 9). This hypothesis has the additional merit of providing a natural explanation for the rather high intensity of the IPES signal in the region -1.0 to 0.0 eV: there should be very little intensity in this gap region for the surfaces phases containing no P atoms, as can be seen from the solid curve. The P-terminated InP(001)-(2×4) surface, in contrast, has a smaller gap than InP(001)-S, and therefore exhibits a sizable signal in the -1.0 to 0.0 eV range. This intensity ledge, together with the broad band from 2.5 to 5.0 eV, are therefore consistent with the hypothesis that the sample contains the InP(001)-P-(2×4)-reconstructed phase as well.

IV. CONCLUSION

We have analysed the published PES and IPES experimental results for the S-passivated InP(001) surface using theoretical calculations for various surface structures which are energetically possible. In this analysis we have borne in mind the fact that the InP(001)-S surface can change its surface composition and structure under annealing, as shown by core-level spectroscopy and by total-energy calculations. Our conclusion is that the experimental results are consistent with a theoretical spectrum obtained from surfaces containing an admixture of several possible phases which could occur under thermal annealing. Some of the broad features in the experimental PES spectrum of Si(111) were discussed in terms of the effect of surface imperfections or local annealing to form 7×7 patches. It is felt that further theoretical and experimental study of the InP(001)-S surface would have to await the availability of better characterized surfaces. However, all the presently-available evidence – Raman, CLS, PES, IPES etc.– except LEED, seem to be consistent with our picture of the as-prepared and moderately-annealed surfaces being a 2×2-reconstruction, essentially S₂SS for the former and mostly (SP)₂ for the latter.

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FIG. 1. (a) Top view of the fully-relaxed, fully-S-covered InP(001) S₂SS surface. The atom species are identified in the z -direction ([001]) layer sequence shown in (b). The x and y directions are [110] and $\bar{[110]}$, respectively. The atomic positions (Å) are obtained from total energy minimization.

FIG. 2. (a) Top view of the the (SP)₂ structure at half-sulphur/half-phosphorous coverage. (b) Atomic planes in the z -direction. The atomic positions are obtained from total energy minimization.

FIG. 3. IPES from the Si(111) surface. The spectrum (PES) calculated using detailed Kohn-Sham matrix elements is shown as the full line, while the dashed line gives the result of a DOS calculation.

FIG. 4. PES from the Si(111) surface. Experimental results for the (2×1) structure is shown as a solid line. The theoretical results for the 16-layer 2×1 slab (dashed lines) and for the bulk Si(111) crystal (dot-dashed line) are shown.

FIG. 5. The solid curve labeled "7x7-aver" in the top panel is the average over small-angle (0–10 deg.) contributions from experimental angle-resolved PES shown in the bottom panel.

FIG. 6. Experimental (squares) and theoretical (lines) PES from the InP(001)S surface. The secondary electron background has been subtracted from the experimental data. (a) The individual PES spectra from the two surface phases considered in the text, namely S₂SS (full line) and (SP)₂ (dashed line), as well as from bulk InP (dotted line). (b) The full line is a composite spectrum for a surface containing a mixture of 30% S₂SS and 70% (SP)₂.

FIG. 7. Experimental (squares) and theoretical (full line) IPES from the InP(001)S surface. Experimental data for the P-terminated InP(001)-(2×4), which is free of sulphur and produced in higher-temperature anneals, is also shown (dashed curve).